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Development of Statistics and Limits for DMR-QA (Data Monitoring Report-Quality Assurance) Studies and Summary of Experience in DMR-QA Study 2

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DEVELOPMENT OF STATISTICS AND LIMITS FOR DMR-QA STUDIES AND SUMMARY OF EXPERIENCE IN DMR-QA STUDY 2

by

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16. ABSTRACT
The self-monitoring data generated by permit holders under the National Pollution Discharge Elimination System (NPDES) and periodically reported to the U.S. Environmental Protection Agency (USEPA) in a Data Monitoring Report (DMR), are an important basis for regulatory and enforcement decisions. In the interest of better quality, USEPA's Office of Water Enforcement (OWE) became interested in establishing a quality assurance (QA) program for DMR data.

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INTRODUCTION

Under the National Pollution Discharge Elimination System (NPDES), permit holders generate self-monitoring data and periodically report it to the U.S. Environmental Protection Agency (USEPA) in a Data Monitoring Report (DMR). The data in these reports are an important basis for regulatory and enforcement decisions. In the pursuit of better quality in these data, USEPA's Office of Water Enforcement (OWE) worked with the Environmental Monitoring and Support Laboratory located in Cincinnati, Ohio (EMSL-CI) to establish a quality assurance (QA) program for DMR data. There are four functional levels required for a successful DMR-QA program:

1. National coordination provided by OWE;

2. Laboratory performance evaluation studies conducted by EMSL-CI;

3. Local coordination, follow-up contacts, and on-site laboratory inspections provided by the responsible USEPA regional office or delegated state primary office;

4. Permittee participation in each study and cooperation to resolve any analytical problems that may be identified.

EMSL-CI agreed to conduct the DMR-QA Studies because of its responsibility for conducting performance evaluation (PE) studies on water laboratories as part of the USEPA Mandatory Quality Assurance Program. Besides DMR-QA Studies, EMSL-CI conducts other studies for drinking water and general water laboratories; a total of six studies this fiscal year. The DMR-QA studies are the largest, involving about 7300 major NPDES permittees, but the other studies each involve from 250 to 1000 laboratories. Over the last eight years, EMSL-CI has completed a total of 24 major laboratory PE studies.

The structure of the different studies is made as uniform as possible to reduce confusion, increase efficiency and minimize the administrative resources required. During a PE study, each participant receives a set of stable sample concentrates in sealed glass ampuls, a data reporting form, and appropriate instructions. Each laboratory produces the study samples by diluting a measured quantity of each concentrate to volume with reagent water, then analyzes them using its routine analytical procedure. The completed form is sent to USEPA for evaluation, and a fully detailed report is returned to each participant. The responsible state or USEPA office follows up with laboratories that demonstrate problems.

The effectiveness of these studies depends upon two things: the acceptance limits must properly identify data resulting from substandard analytical work, and laboratories submitting unacceptable results must either improve their performance or be excluded from producing further DMR data.

DEVELOPMENT OF ACCEPTANCE LIMITS

USEPA's objective in developing acceptance limits is to be able to distinguish between data from analytical systems operating within state-of-the-art capabilities and data resulting from substandard performance. A statistical confidence interval at an appropriate significance level is clearly suitable if acceptable data have a normal distribution and if proper estimates of the arithmetic mean and standard deviation are available. Since there are no independent sources of comparable information, it is necessary to investigate the data from the previous and current USEPA studies themselves to establish a basis for the desired limits.

Estimating the Study Statistics

For each analyte in a sample, basic descriptive statistics are estimated from the data submitted by the participating USEPA and state laboratories, usually numbering over 100. The statistics are estimated from these data because USEPA is more familiar with the operating characteristics of these laboratories and judges them to be generally capable of producing data representative of approved analytical procedures, when properly applied. The statistical report for each analyte includes the following:

1. Identification of obvious outliers in the data set;

2. Traditional and robust estimates of the mean ($\bar{X}$) and standard deviation (S) from the retained data;

3. Tests of normality for the retained data;

4. A histogram of the retained data; and

5. A complete listing of the USEPA and state data, with the obvious outliers noted.

Specific details on all parts of this statistical report can be found in Britton (1982).

The robust estimates of the mean and standard deviation developed above, become the basic statistical representation of data generated by an analytical system operating properly. Robust estimates are calculated from an ordered set of the retained data, using a 25 percent Winsorizing procedure to estimate the mean as described by Dixon and Massey (1969), and basic properties of a normal distribution to estimate the standard deviation.

After the retained data have been arranged in ascending order, $X_1 \leq X_2 \leq \ldots \leq X_n$, the Winsorized estimate of the mean is calculated as:

$$\bar{X} = K(X_K) + \sum_{i=K+1}^{n-K} X_i + K(X_{n-K+1}) \quad /n, \qquad (1)$$

where

K = (the greatest integer portion of n/4) + 1.

The robust estimate of the standard deviation is calculated from the interquartile distance across the middle 50 percent of the ordered retained data. Assuming an underlying normal distribution, this distance is equivalent to 1.349 standard deviations. The calculation is:

$$S = \left(\frac{1}{1.349}\right) X_{n-J+1} - X_J + \left(J - \frac{n}{4} - .5\right)\left((X_J - X_{J-1}) + (X_{n-J+2} - X_{n-J+1})\right), \qquad (2)$$

where

J = (the greatest integer portion of (n+1)/4) + 1.

Developing Regressions from Previous Study Statistics

Where appropriate background statistics are available, experience indicates that reasonable estimates of the mean and standard deviation for the current study samples can be made from linear regressions generated from the historical statistics. These linear regressions, for $\overline{X}$ versus true value (T) and S versus T, are achieved by using the customary least-squares algorithm to fit:

$$\frac{\overline{X}}{T} = a + b\left(\frac{1}{T}\right) \quad \text{and} \quad \frac{S}{T} = c + d\left(\frac{1}{T}\right) \tag{3}$$

which can then be converted to the desired relationships by multiplying through by T, giving:

$$\overline{X} = aT + b \quad \text{and} \quad S = cT + d. \tag{4}$$

This technique is a weighted linear fit and leads to a minimization of the sum of the square of the residuals as a percentage of the true value associated with each residual. If the least-squares algorithm is used to fit the desired relationship directly, the statistics for the samples with high true values will tend to dominate the regressions and can produce incorrect estimates of the mean and standard deviation for samples with low true values. After a comparison of results with traditional linear, quadratic, cubic and power curve fits to the historical statistics, it was concluded that the best fit occurred with the weighted linear regression procedure.

Establishing the Limits

Table 1 presents the regression and direct statistical estimates for the DMR-QA Study 2 samples. To establish limits for the study, regression estimates of the mean and standard deviation are compared with the statistics calculated from the study data. If the two sets of statistical estimates agree reasonably well, the regression estimates are used as the basis for acceptance limits because: they are independent of the data to be evaluated; there is more information behind them; and the regression equations force a smooth, logical relationship between samples with different concentrations.

If the predicted statistics (mean or standard deviation or both) differ from the corresponding sample statistics, there must be a thorough investigation to establish cause. Such a problem may result from the use of regression equations to estimate statistics at true values outside the concentration range from which the regression were developed, use of incorrect true values or a significant change in the way the samples were made. If suitable regression estimates cannot be developed, the study statistics themselves must be used as the basis for acceptance limits.

PERFORMANCE EVALUATION REPORTS

Once appropriate statistics are available, it is a simple matter to calculate the 95 and 99 percent confidence limits to be used as warning and acceptance limits, respectively, and proceed with evaluating the study data. Figures 1 and 2 are the final report forms developed for the two sets of concentrates used in Study 2. An individual report is generated for each participant which shows the data reported, the related true values and limits, and an evaluation judgment for each reported value based upon its relationship to the limits. Each participant receives a copy of their report, and a copy is sent to the responsible USEPA regional and state offices for follow-up contact, as necessary, to resolve unacceptable performance.

EXPERIENCE IN DMR-QA STUDY 2

Performance of the 5216 major NPDES dischargers participating in DMR-QA Study 2 is given on the last line of Table 2. Only one of the two sets of study concentrates was analyzed for each participating discharger. The remainder of Table 2 summarizes the performance of other groups of laboratories that independently analyzed the same samples and were judged against the same limits.

Cross comparisons within Table 2 provide some prospective for evaluating performance by the discharger laboratories. For example, results for the discharger laboratories are virtually identical to results for the independent group of USEPA contract laboratories, indicating similar capabilities between the non-USEPA/non-state laboratories contributing so much of USEPA's data. At the same time, much better performance of the USEPA and state laboratory groups makes it quite clear that there is considerable room for improvement in the performance of both groups of non-USEPA/non-state laboratories.

CONCLUSIONS

Results from these studies show the potential for improvement in the analytical capability of the major non-USEPA/non-state laboratories which produce so much of USEPA's water data. Whether any improvement actually occurs, however, depends entirely upon the commitment of the responsible state and USEPA enforcement offices, as well as the major NPDES dischargers, to make the changes necessary to improve the quality of monitoring data.

TABLE 1: BACKGROUND STATISTICS FOR DMR-QA STUDY 2

Parameter	Units	Concentrate 1 TV	n	$\bar{X}$	S	Concentrate 2 TV	n	$\bar{X}$	S
Al	µg/L	503	46	519.[a] 494.[b]	52.9 35.6	1260	45	1259 1180	108 88.0
As	"	79.6	49	78.7 82.9	11.3 6.97	302	49	297 312	41.6 23.4
Be	"	552	30	549 530	31.8 25.9	719	30	715 686	41.1 25.9
Cd	"	113	64	N/A 113	N/A 7.41	200	63	N/A 200	N/A 10.0
Cr	"	164	63	161 161	16.2 14.8	470	62	461 475	45.6 27.4
Co	"	867	33	N/A 821	N/A 41.0	122	34	122 121	7.79 7.41
Cu	"	669	67	660 660	37.5 28.7	892	68	879 883	49.6 38.2
Fe	"	1990	59	1981 1933	133 66.7	1260	60	1255 1230	85.3 46.7
Pb	"	286	62	285 280	20.5 17.0	108	63	108 108	9.12 12.4
Mg	"	126	60	125 126	9.22 7.41	299	60	298 300	19.8 14.8
Hg	"	45.0	54	42.1 44.1	9.52 6.60	12.7	54	11.9 12.4	2.72 2.22

N/A - Not Available

a Statistical estimates on the first line for each parameter have been generated from linear regressions based upon USEPA and state statistics from previous studies.

b Statisti s on the second line for each parameter have been estimated directly from USEPA and state laboratory analyses of the study samples.

TABLE 1: BACKGROUND STATISTICS FOR DMR-QA STUDY 2
(continued)

		Concentrate 1				Concentrate 2			
Parameter	Units	TV	n	$\bar{X}$	S	TV	n	$\bar{X}$	S
Ni	µg/L	672	57	663 666	52.4 37.1	877	56	865 877	67.9 37.8
Se	"	15.0	47	14.2 13.4	2.49 2.22	37.1	46	35.1 34.2	5.80 5.93
V	"	1860	28	1872 1909	163 140	240	25	240 248	25.6 15.6
Zn	"	1000	64	991 997	43.1 30.0	1490	66	1476 1504	62.7 56.3
pH	Std.	5.45	78	5.44 5.47	.0398 .0445	6.45	80	6.45 6.48	.0532 .0445
TSS	mg/L	31.6	67	N/A 31.6	N/A 2.74	44.2	66	N/A 44.2	N/A 2.97
Oil & grease	"	18.0	54	17.7 17.2	1.86 2.22	6.0	55	5.86 6.07	1.00 1.09
Ammonia-N	"	0.663	71	.661 .677	.0441 .0426	2.51	68	2.51 2.49	.135 .115
Nitrate-N	"	4.30	70	4.27 4.25	.181 .148	0.352	69	.351 .350	.0213 .0221
TKN	"	7.69	60	7.53 7.63	.486 .500	13.3	60	13.0 13.1	.798 .815
T. Phosphorus	"	0.515	71	.526 .530	.0266 .0208	0.911	68	.929 .931	.0407 .0371
Orthophosphate	"	2.19	65	2.18 2.18	.0439 .0760	3.69	65	3.67 3.68	.0711 .122
COD	"	40.2	63	38.9 38.0	3.63 4.26	92.0	65	88.5 89.6	5.94 6.39
TOC	"	15.8	28	15.7 15.7	1.72 1.00	36.1	29	35.6 35.5	3.30 2.22
5-day BOD	"	26.7	68	26.7 26.8	4.10 2.93	61.1	70	61.2 61.7	9.03 5.78

N/A Not Available

FIGURE 1. BLANK REPORT FORM FOR THE "CONCENTRATE 1" SET OF SAMPLES IN DMR-QA STUDY 2

PERFORMANCE EVALUATION REPORT
NPDES STUDY NUMBER 2

PERMITTEE:

PARAMETER	REPORT VALUE	TRUE VALUE	ACCEPTANCE LIMITS	WARNING LIMITS	PERFORMANCE EVALUATION
TRACE METALS IN MICROGRAMS PER LITER:					
ALUMINUM		503.	376.-663.	412.-626.	
ARSENIC		79.6	48.3-109.	56.0-101.	
BERYLLIUM		552.	442.-618.	464.-595.	
CADMIUM		113.	93.3-133.	98.2-128.	
CHROMIUM		164.	118.-204.	128.-193.	
COBALT		867.	681.-961.	717.-925.	
COPPER		669.	559.-760.	584.-735.	
IRON		1990.	1630.-2340.	1710.-2250.	
LEAD		286.	230.-339.	243.-326	
MANGANESE		126.	101.-150.	107.-144.	
MERCURY		45.0	16.2-67.9	22.7-61.4	
NICKEL		672.	522.-803.	557.-768.	
SELENIUM		15.0	6.69-20.2	8.40-18.5	
VANADIUM		1860.	1410.-2330.	1530.-2210.	
ZINC		1000.	875.-1110.	904.-1080.	
MISCELLANEOUS ANALYSES:					
PH (UNITS)		5.45	5.32-5.56	5.35-5.53	
TOTAL SUSPENDED SOLIDS (MG/L)		31.6	24.3-38.9	26.1-37.1	
OIL AND GREASE (MG/L)		18.0	11.2-23.1	12.7-21.6	

FIGURE 1. BLANK REPORT FORM FOR THE "CONCENTRATE 1" SET OF SAMPLES IN DMR-QA STUDY 2 (continued)

PERFORMANCE EVALUATION REPORT
NPDES STUDY NUMBER 2

PERMITTEE:

PARAMETER	REPORT VALUE	TRUE VALUE	ACCEPTANCE LIMITS	WARNING LIMITS	PERFORMANCE EVALUATION
NUTRIENTS IN MILLIGRAMS PER LITER:					
AMMONIA-NITROGEN		0.663	.544-.779	.573-.750	
NITRATE-NITROGEN		4.30	3.79-4.75	3.91-4.63	
KJELDAHL-NITROGEN		7.69	6.30-8.96	6.63-8.63	
TOTAL PHOSPHORUS		0.515	.455-.597	.473-.579	
ORTHOPHOSPHATE		2.19	1.98-2.38	2.03-2.33	
DEMANDS IN MILLIGRAMS PER LITER:					
COD		40.2	26.6-49.3	29.4-46.5	
TOC		15.8	11.0-20.5	12.2-19.2	
5 DAY BOD		26.7	15.9-37.5	18.6-34.9	

FIGURE 2: BLANK REPORT FORM FOR THE "CONCENTRATE 2" SET OF SAMPLES IN DMR-QA STUDY 2

PERFORMANCE EVALUATION REPORT
NPDES STUDY NUMBER 2

PERMITTEE:

PARAMETER	REPORT VALUE	TRUE VALUE	ACCEPTANCE LIMITS	WARNING LIMITS	PERFORMANCE EVALUATION
TRACE METALS IN MICROGRAMS PER LITER:					
ALUMINUM		1260.	887.-1470.	961.-1400.	
ARSENIC		302.	185.-410.	214.-381.	
BERYLLIUM		719.	601.-829.	630.-799.	
CADMIUM		200.	173.-226.	180.-220.	
CHROMIUM		470.	338.-583.	369.-552.	
COBALT		122.	100.-143.	106.-138.	
COPPER		892.	746.-1010.	780.-979.	
IRON		1260.	1030.-1480.	1080.-1430.	
LEAD		108.	75.1.-142.	83.4.-133.	
MANGANESE		299.	245.-351.	258.-338.	
MERCURY		12.7	4.51-19.3	6.39-17.4	
NICKEL		877.	682.-1050.	728.-1000.	
SELENIUM		37.1	18.3-50.2	22.3-46.2	
VANADIUM		240.	168.-312.	187.-293.	
ZINC		1490.	1340.-1670.	1380.-1630.	
MISCELLANEOUS ANALYSES:					
PH (UNITS)		6.45	6.31-6.60	6.35-6.56	
TOTAL SUSPENDED SOLIDS (MG/L)		44.2	36.3-52.1	38.3-50.1	
OIL AND GREASE (MG/L)		6.0	3.15-8.99	3.87-8.26	

FIGURE 2: BLANK REPORT FORM FOR THE "CONCENTRATE 2" SET OF SAMPLES IN DMR-QA STUDY 2 (continued)

PERFORMANCE EVALUATION REPORT
NPDES STUDY NUMBER 2

PERMITTEE:

PARAMETER	REPORT VALUE	TRUE VALUE	ACCEPTANCE LIMITS	WARNING LIMITS	PERFORMANCE EVALUATION
NUTRIENTS IN MILLIGRAMS PER LITER:					
AMMONIA-NITROGEN		2.51	2.15-2.87	2.24-2.78	
NITRATE-NITROGEN		0.352	.294-.408	.308-.393	
KJELDAHL-NITROGEN		13.3	10.9-15.3	11.5-14.7	
TOTAL PHOSPHORUS		0.911	.820-1.04	.847-1.01	
ORTHOPHOSPHATE		3.69	3.36-4.01	3.44-3.93	
DEMANDS IN MILLIGRAMS PER LITER:					
COD		92.0	72.6-107.	76.8-102.	
TOC		36.1	26.6-44.7	28.9-42.4	
5 DAY BOD		61.1	37.4-85.0	43.2-79.2	

TABLE 2: COMPARATIVE PERFORMANCE ON THE DMR-QA STUDY 2 SAMPLES

Participant Group	Concentrate 1			Concentrate 2		
	Number of Labs	Data Beyond Warning Limits (%)	Data Beyond Acceptance Limits (%)	Number of Labs	Data Beyond Warning Limits (%)	Data Beyond Acceptance Limits (%)
USEPA Labs	20	6	4	20	8	4
State Labs	112	15	10	112	14	9
USEPA Contractors	139	27	22	139	26	21
DMR-QA Study 2	2659	28	22	2557	27	21

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